Förster-type nonradiative energy transfer directed from colloidal quantum dots to epitaxial quantum wells for light harvesting applications

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Abstract: We report on Förster-type nonradiative energy transfer directed from CdSe/ZnS core/shell quantum dots to InGaN/GaN quantum wells with 69.6% efficiency at 1.527 ns^{-1} rate at room temperature for potential light harvesting and solar cells applications.

OCIS codes: (260.2160) Energy transfer; (160.4236) Nanomaterials; (230.5590) Quantum-well, -wire and -dot devices

III-Nitrides exhibit potential advantages important for photovoltaics including high carrier mobility, radiation resistance and direct band gap covering almost the entire visible spectrum [1]. Today high-end inorganic solar cells based on quantum well (QW) absorbers typically utilize a *p-i-n* diode architecture. QWs placed in the *i*-region absorb incident photons and generate excitons. Subsequently, built-in electric field of the diode disassociates these photogenerated excitons and separates the electron and hole pairs. However, it is not desirable to incorporate a very thick layer of QW absorbers in the diode, for this comes at the cost of reduced built-in electric field to separate and collect the charges. In the case of thin absorbing QW layers, though, low light absorption may limit the efficiency of this type of solar diodes [2]. Moreover, undesired absorption of the incoming photons possibly in the top contact layer, if any, may also contribute to the reduction of solar conversion efficiency. As an alternative way, we investigate and demonstrate a hybrid system of colloidal core/shell quantum dots (QDs) integrated with epitaxial InGaN/GaN QWs to facilitate incoherent dipole-dipole coupling and excitonic energy conversion between them [3]. In this system, QDs donate photogenerated excitons to the nearby QWs via Förster-type nonradiative resonance energy transfer (NRET) as an extra exciton generation pathway in addition to the direct photon absorption of QWs. Favorably, through this hybrid configuration, the absorption cross-section of the quantum wells can be enhanced as a result of the additional exciton harvesting in the quantum dots, and the electron-hole pairs that would be otherwise wasted in the top contact layer may be decreased [4]. The feasibility of this type of NRET-based light harvesting into InGaN/GaN QWs offers new possibilities for InGaN material system important for future photovoltaics.

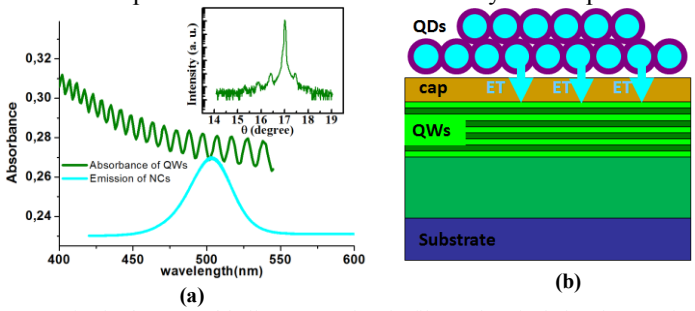

Figure 1. (a) Photoluminescence of CdSe/ZnS core/shell quantum dots in film and optical absorbance of InGaN/GaN quantum wells along with their X-ray diffraction measurement (given in the inset), and (b) schematic representation of the hybrid system consisting of dipole-dipole coupled quantum dots and quantum wells.

In our hybrid system we use cyan-emitting colloidal CdSe/ZnS quantum dots and green-emitting epitaxial InGaN/GaN multi-quantum wells. CdSe/ZnS dots exhibit a photoluminescence emission peak of 490 nm in toluene, and have a concentration of 15.85 nmol/ml with a size dispersion of <5%. We prepare our InGaN/GaN epi-wafer by growing 3.5 μm thick, n-doped GaN on top of the polished sapphire substrate. We then continue with 5 InGaN/GaN well/barrier layers and finally finish our epitaxial structure with a few monolayers of undoped GaN capping layer. The well and barrier thicknesses are around 89 nm according to the X-ray diffraction measurement (XRD) shown in

the inset of Figure 1(a). These QWs posses an indium mole fraction of 72% in the well, resulting in a photoluminescence peak around 512 nm presented in Figure 1(a). The absorption of QWs and emission of QDs overlap sufficiently well for strong dipole-dipole coupling in the hybrid system to yield efficient NRET as depicted in Figure 1(a). For our hybrid system, we integrate our quantum dots on top of this wafer as sketched in Figure 1(b). Here the center-to-center distance is predicted to be ~3.8 nm (~1 nm QW center to GaN capping layer + ~1 nm GaN capping layer thickness + ~1.8 nm ligand and QD radius). Since our QWs are electronically uncoupled due to their thick shell barrier layers (ca. 16 nm), farther QWs except for the nearest ones do not contribute to the NRET process, unless they contribute to a cascaded NRET that eventually makes it to QWs.

To investigate the NRET process from QDs to QWs, we use time-resolved spectroscopy. For that, we utilize a laser head emitting at 375 nm to excite QDs and QWs, and employ a photon multiplier tube (PMT) with a calibrated time sampling rate of 64 ps between two adjacent data points. In Figure 2(a), the time-resolved decay at 460 nm is shown and the photoluminescence decay curve of the hybrid sample at 460 nm decreases faster with respect to the only cyan-emitting QDs because, in addition to the recombination in QDs, the excitons generated in donor quantum dots are transferred to and collected at the acceptor quantum wells in the hybrid structure. To understand the decay rates and energy transfer efficiency, we fit decays by using a single exponential as given in Figure 2. The rate of only QDs (i.e., k_{QD}) corresponds to 0.665 ns^{-1} and the rate of the hybrid system QD+QW (i.e., k_{QD+QW}) is equal to 2.192 ns^{-1}. By using these rates, we calculate the NRET rate $k_{NRET} = k_{QD+QW} - k_{QD}$= 1.527 ns^{-1}. As a result, the hybrid system accomplishes an NRET efficiency of 69.6% ($\eta=k_{NRET}/(k_{NRET}+k_{QD})= k_{NRET}/k_{QD+QW}$), meaning that most of the excitons generated in QDs are transferred to nearby QWs. To check NRET we additionally examine the time-resolved behaviour of our hybrid system for the acceptor emission at 540 nm to understand the transient QW dynamics (where the emission of the QDs is negligible as shown in Figure 1(a)). In Figure 2(b) the time-resolved photoluminescence of the hybrid sample at 540 nm exhibits a slower decay with respect to the only green-emitting QWs because these acceptor wells are additionally fed with the transferred energy from the donor dots in the hybrid structure with respect to the only green-emitting wells. To observe NRET in the acceptor emission, the fluorescence dynamics of the hybrid system is subtracted from the dynamics of the only quantum wells and the difference curve is presented in the inset of the Figure 2(b). Here this behavior is due to the exciton injection from the QDs to the QWs [5]. One possible question here is whether there is also Dexter-type charge transfer process. Since in our core/shell heteronanocrystals ZnS barriers provide full electronic isolation and completely prevent tunneling of the electron and hole wavefunctions, this eliminates the possibility of Dexter-type transfer. Thus, this transfer needs to take place as a result of nonradiative energy transfer from quantum dots to quantum wells. As a remark, in the inset of Figure 2(b) the lifetime increase for the hybrid sample with respect to the only green-emitting QWs is not as pronounced because only the top QW is nonradiatively pumped and the other remaining four QWs are radiatively pumped.

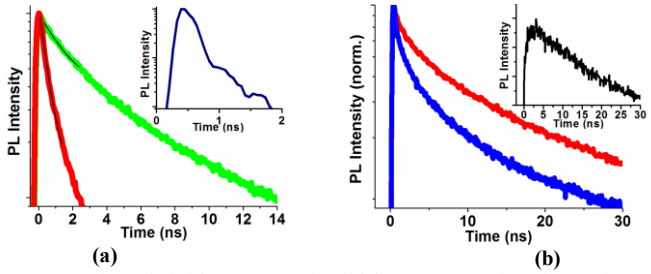

Figure 2. (a) Time-resolved spectroscopy of our hybrid system (red solid line) compared against only quantum dots (green solid line), both measured at the emission wavelength of 460 nm. The solid black lines are the fitted curves. Inset shows the response decay of the excitation laser, and (b) time-resolved spectroscopy of our hybrid system (red solid line) compared against only quantum wells (blue solid line) both measured at the emission wavelength of 540 nm. Inset shows the difference between the decay dynamics of hybrid system and only quantum wells (black solid line).

To summarize, we presented nonradiative Förster-type resonance energy transfer from colloidal quantum dots to epitaxial quantum wells for III-nitride based photovoltaic applications, where this hybrid scheme achieved an NRET efficiency of approximately 69.6% and an NRET rate of 1.527 ns^{-1}.

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References

[1] O. Jani, I. Ferguson, C. Honsberg, and S. Kurtz, Appl. Phys. Lett. **91**, 132117 (2007).

[2] J. Wu et al., J. Appl. Phys. **94**, 6477 (2003).

[3] S. Nizamoglu, E. Sari, J.-H. Baek, I.-H. Lee and H. V. Demir, Physica Status Solidi (RRL) - Rapid Research Letters, **4**, 178-180 (2010).

[4] M. Achermann, M. A. Petruska, S. A. Crooker, and V. I. Klimov, J. Phys. Chem. B 107, 13782 (2003).

[5] S. Chanyawadee, P.G. Lagoudakis, R.T. Harley, M.D.B. Charlton, D.V. Talapin, and S. Lin, Adv. Mat. **22**, 602 (2010).